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(54) Title: EMULSIFIERS FOR OIL BASED DRILLING FLUIDS

(57) Abstract

An oil-based well-working fluid comprising a) an emulsifier comprising the reaction product of i) one or two moles of an amide-amine or a hydroxyalkyl amide (herein defined as component i); with ii) one to five moles of a dicarboxylic acid or an acid anhydride [preferably an acid anhydride] (herein defined as component ii); b) a hydrocarbon drilling oil; and c) a sodium, calcium or magnesium brine.

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EMULSIFIERS FOR OIL BASED DRILLING FLUIDS

The invention relates to the preparation of improved emulsifier additives for use in oil based drilling fluids and to products so obtained.

In the drilling of wells by the rotary drilling technique, drilling fluid is circulated from tanks at the wellhead down the inside of the drill-pipe, through the bit and back up the annulus. On reaching the wellhead the fluids are subjected to a number of treatments designed to remove gases or solid materials such as drilled cuttings, sand, colloidal material, etc. from the fluid before being returned to the well via the mud tanks. During the course of this circulation the properties of the drilling fluid change, due to a number of factors such as ingress of water or fine solids or temperature degradation of the components of the fluid. As a result the fluid is treated to regenerate the required properties and this treatment generally involves the addition of chemicals.

As the total reserves of oil diminish, it has become necessary to drill in areas which were previously inaccessible due to technological or economic difficulties. This has led to the development of increasing sophisticated drilling fluids and in particular to the widespread use of oil-based fluids. These have a number of advantages over conventional water-based drilling fluids. Oil-based fluids are less prone to thermal degradation than water-based fluids and as a result are used to drill deep hot holes.

In order to drill effectively from offshore platforms, economics dictate that as much of the field as possible should be exploited from each platform. This has led to an increase in the number of deviated wells and also to an increase in the maximum angle of deviation. The latter causes a marked increase in the torque required to maintain rotation of the drill-string. Oil-based drilling fluids exhibit extremely good lubricity compared with water based fluids and have proved particularly effective in the drilling of deviated wells.

Drilling through hydratable shales has proved troublesome due to the swelling and sloughing of these formations on contact with aqueous drilling fluids. The problem is common throughout the world and not only leads to wellbores which are out of gauge but also to torgue and stuck-pipe problems. Oil-based drilling fluids do not affect most shales and are ideally suited to drilling through these formations.

In order to achieve a maximum production rate from a well it is important that the fluid, used to penetrate the production zone, and the subsequent completion fluid do not damage the formation.

Oil- based drilling fluids are designed to give a filtrate consisting only of oil and since this is essentially native to the production formation, it does not lead to a reduction in permeability. Aqueous fluids can cause loss of productivity due to pore contraction and blocking as a result of the hydration of clays.

Oil-based well-working fluids or muds can be classified as true oil muds and invert emulsion muds. The former contain only a small amount of water whilst the latter may contain up to 40 % or more water as the dispersed phase of an invert (water-in-oil) emulsion. Each of these fluids may contain a number of additives such as emulsifiers, viscosifiers, fluid loss reducing additives and various inorganic salts.

Emulsifiers are required to form a stable dispersion of water droplets in an oil phase (invert emulsion mud) and to maintain any

solids, for example weighting materials such as barytes or solids encountered during drilling in an oil-wet state.

According to the invention, there is provided an emulsifier composition comprising

1) 80-99 % of the reaction product (hereinafter defined as component 1) of

i) one or two moles of an amide-amine having at least one free amino group or hydroxy alkyl amide having at least one hydroxy group (herein defined as component i); component i) being free of any imidazoline groups; and

ii) one to five moles of a dicarboxylic acid or an acid anhydride (preferably an acid anhydride) (hereinafter defined as component ii); and

2) 1-20 % of one of more compounds selected from dimer acids, C_{8-22} alkyl benzenesulphonic acids, naphthenic acids, tall oil, oxidised tall oil, C_{4-22} alkylphenol ethoxylates, straight chain alcohol ethoxylates, carboxymethylates and sulphosuccinates, (hereinafter defined as component 2)
all percentages being based on the weight of actives in the emulsifiers.

Preferably an emulsifier according to the invention comprises 20-80 % of components 1 and 2 and 80-20 % of one or more solvents.

Preferred solvents include hydrocarbon paraffins (e.g. oils) such as diesel oil. Such solvents can be hydrocarbon drilling oil. Preferred components 1 contain at least one free acid group.

Preferred C_{4-22} alkylphenol ethoxylates are t.butyl-, nonyl- and iso octyl - phenol ethoxylated with 4 to 15 moles of ethylene oxide.

Preferred C_{8-22} alkyl benzene sulphonic acids are dodecylbenzene sulphonic acids.

Preferred straight chain alcohol ethoxylates are C_{1-12} alkanols ethoxylated with 4 to 15 moles of ethylene oxide.

Preferred carboxymethylates are reaction products of an ethoxylated and/or propoxylated alcohol and chloroacetic acid, e.g. 1 mole C_{8-22} alcohol ethoxylated with 4-12 moles of ethylene oxide, reacted with 1 mole of chloroacetic acid.

Preferred sulphosuccinates are reaction products of 1-2 moles of an alcohol or ethoxylated and/or propoxylated alcohol with 1 mole of maleic anhydride further reacted with sodium sulphite, e.g. 2 moles ethylhexanol with 1 mole of maleic anhydride and 1 mole of sodium sulphite.

Further according to the invention, there is provided an oil-based well working fluid comprising

a) 1-5 % of an emulsifier composition according to the invention
b) 40-97 % of a hydrocarbon drilling oil; and
c) 2-60 % of a sodium, calcium or magnesium brine,

all percentages being by weight of the well working fluid.

Preferably the hydrocarbon drilling oil is diesel oil or a low toxicity drilling oil. Such drilling oils are also known as oil muds as described in "The Oilman" April, 1983 pages 45-49 in an article entitled "Non-polluting Oil Muds" by J. Hall and P. Grange, the contents of which are incorporated herein by reference.

Preferably the brine is a calcium brine.

Well working fluids according to the invention may also include one or more compounds selected from the following: lime, viscosifiers (e.g. oleophilic bentonites), weighting agents (such as barytes), further fluid loss additives, dispersants, stabilizers and lost

circulation additives (such as attapulgites).

Preferably when component i) is an amide-amine, it is the reaction product of

a) ethylene diamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

b) diethylene triamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

c) triethylene tetraamine with an C_{1-22} alkanoic acid, C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

d) tetraethylene pentamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fattv acid, a trimer fatty acid or a monoether polyacid.

Preferably in the reaction to prepare the above reaction products, 1 to 3 moles of amine is used, depending on the number of carboxy groups present.

Preferably in the reaction to prepare the above reaction products, 1 to 4 moles of acid is used, depending on the amine present.

More preferably when component i) is an amide-amine it is the product of any one of formulae III to VII (in any of the isomeric forms)

$$R_{30}-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2\overset{\overset{\overset{O}{\|}}{C-R_{30}}}{N}CH_2CH_2-\overset{\overset{\overset{O}{\|}}{C-R_{30}}}{N}-CH_2CH_2NH_2 \qquad (III)$$

$$R_{30}-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2NHCH_2CH_2NH-\overset{\overset{O}{\|}}{C}-R_{30} \qquad (IV)$$

$$R_{30}-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2NH_2 \qquad (V)$$

$$R_{30}-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2NH-CH_2CH_2NH_2 \qquad (VI)$$

$$R_{30}-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2\underset{\overset{|}{\underset{\overset{\|}{O}}{C}-R_{30}}}{N}CH_2CH_2\underset{\overset{|}{\underset{\overset{\|}{O}}{C}-R_{30}}}{N}CH_2CH_2\underset{\overset{|}{\underset{\overset{\|}{O}}{C}-R_{30}}}{N}CH_2CH_2NH_2 \qquad (VII)$$

where each R_{30} independently, is hydrogen, C_{1-21} alkyl or C_{2-21} alkenyl; or component i) when an amide-amine is preferably the product of reacting

1 to 3 moles of ethylene diamine with 1 mole of a dimer fatty acid or a trimer fatty acid ; or

1 to 3 moles of diethylene triamine with 1 or 2 moles of a dimer fatty acid or a trimer fatty acid; or

1 to 3 moles of triethylene tetraamine with 1 to 3 moles of an a dimer fatty acid or a trimer fatty acid ; or

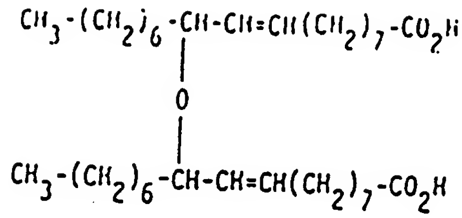
1 to 3 moles of tetraethylene pentamine with 1 to 4 moles of a dimer fatty acid or a trimer fatty acid.

The reaction products of component i) are known or may be made from known compounds by known methods.

Preferred C_{1-22} alkanoic acids and/or C_{3-22} alkenoic acids include tall oil fatty acid (which contains oleic acid and linoleic acid).

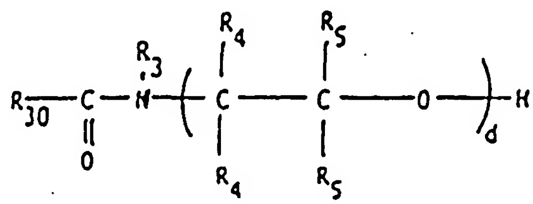
Preferably a dimer fatty acid is of 24 to 44 carbon atoms. Preferably a trimer fatty acid is of 36 to 66 carbon atoms.

Preferred monoether polyacids include oxidised tall oil which contains a compound of the formula VIII

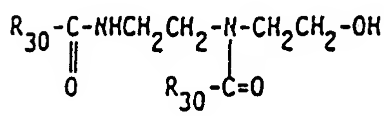


(VIII)

Preferably when component i) is hydroxyalkyl amide it is a compound of formula IX or X

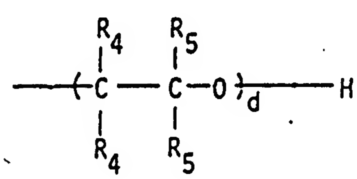


(IX)



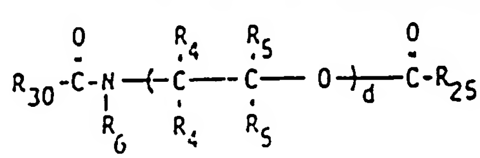
(X)

where R_3 is hydrogen or C_{1-4}alkyl (preferably hydrogen); or R_3 is a group of the formula

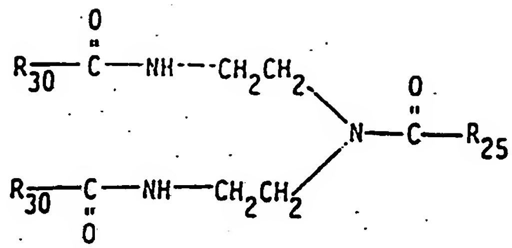


in which
each d, independently, is an integer from 1 to 15 inclusive;
each R_4, independently, is hydrogen or C_{1-4} alkyl; and
each R_5 independently has one of the significances of R_4; and
R_{30} is as defined above.

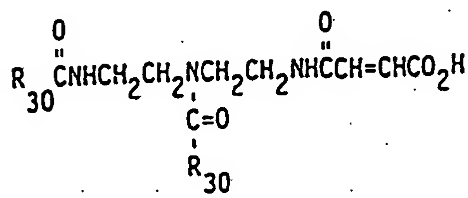
Component 1 (e.g. the reaction products of components i) and ii) is often mixtures of products. Preferably component 1 includes a compound selected from those of formulae XII to XVI (in any isomeric form)



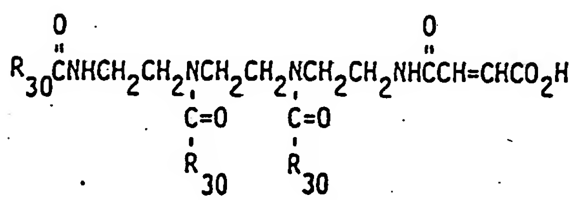
(XII)



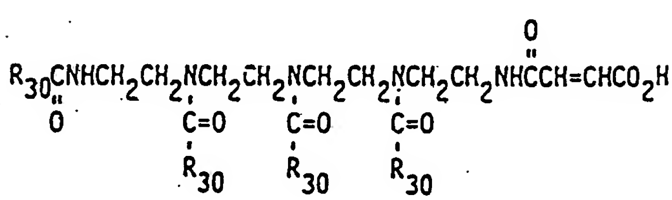
(XIII)



(XIV)

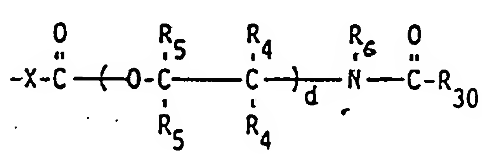


(XV)



(XVI)

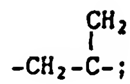
where R_{25} is $-X-CO_2H$ or

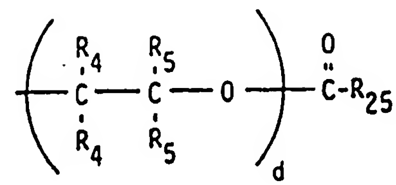


where R_{30} is as defined above;

d is as defined above;

X is a direct bond, C_{1-12}alkylene; C_{2-12}alkenylene; $-CH_2-O-CH_2$;

or 

and R_6 is hydrogen, C_{1-4}alkyl or 

X is preferably X_a where X_a is -CH=CH-.

Preferred dicarboxylic acids of component ii) are of the formula $HOOC-Z-CO_2H$ where Z is a direct bond, C_{1-12}alkylene or C_{2-12}alkenylene; more preferably the dicarboxylic acids of component ii) are selected from itaconic acid, maleic acid, succinic acid, glutonic acid and diglycollic acid.

Preferred acid anhydrides of component ii) are maleic anhydride, succinic anhydride, glutonic anhydride, diglycollic anhydride and itaconic anhydride.

Most preferred components 1 are those of formulae XII and XIII where R_{25} is $-X-CO_2H$ and those of formulae XIII, XIV, XV and XVI.

An emulsifier of a well working fluid according to the invention is present in an amount to give a concentration, preferably of from 1 to 20 pounds per barrel(ppb), more preferably 2-10 ppb, based on the weight of the well working fluid.

The terms "dimer fatty acid" and "trimer fatty acid" as used in this Specification mean, respectively, a dibasic acid resulting from condensation of two molecules of an unsaturated fatty acid or ester (dimerization) and a tribasic acid resulting from condensation of three molecules of an unsaturated fatty acid or ester (trimerization). Such products have been known for many years and have been used commercially since the late 1940's. They are discussed in detail in the monograph entitled "The Dimer Acids - The chemical and physical properties, reactions and applications of polymerized fatty acids", edited by Edward C. Leonard, Humko Sheffield Chemical (1975) of which Chapter 1, "The General Characterization of Dimer Acids", By Berman and Loeb, is incorporated herein by reference.

As discussed in the aforementioned monograph, dimer and trimer fatty acids are commercially prepared by thermal condensation of unsaturated fatty acids in the presence of a clay catalyst, e.g. montmorillonite clay, usually by a Diels-Alder type reaction. Preferred starting materials for the dimer and trimer acids are C_{12-22} alkenyl (preferably straight chain) monomeric fatty acids. A particularly favoured source of such acids is tall oil fatty acid comprising oleic and linoleic acid in admixture with lesser amounts of palmitic and stearic acids and other saturated and unsaturated acids. However, it is also possible to use individual unsaturated acids, such as oleic or linoleic acid.

Commercial processes for producing dimer acids usually result in mixtures which may contain varying amounts of monomeric by-products and starting materials as well as trimer and higher polymeric acids along with the dimer fatty acid. If desired the components of such mixtures may be separated, e.g. by distillation.

A number of compounds of component (i) are described in EP 49494, the contents and preferences of which are incorporated by reference and GB Published Patent Application No. 2,135,321 B the contents and preferences of which are incorporated by reference.

In this Specification for the avoidance of doubt, where any symbol appears more than once in a formula, its significances are independent of one another, unless indicated to the contrary.

Furthermore where any group is capable of being linear or branched, it is linear or branched unless indicated to the contrary.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight and all temperatures are in °C unless indicated to the contrary.

Example 1

103 g of diethylenetriamine is added to 570 g of a commercially available tall oil fatty acid under an atmosphere of nitrogen and the reaction temperature is maintained below 100 °C.

The reaction mixture is then heated to 140°C and 36 g of water is removed by distillation. The reaction is cooled and yields 637 g of a 2:1 amide of crude oleic acid and diethylene triamine.

Under an atmosphere of nitrogen, 637 g of the 2:1 amide prepared above are heated to 80°C and 98 g of maleic anhydride are added at such a rate so as to keep the temperaure below 100°C. When the addition is complete, the reaction is heated to 140°C for two hours. The reaction mixture is then cooled and discharged to yield 416.5 g of a compound of formula 1a

$$\left[R_{30}\text{—CO—NH—}CH_2CH_2\right]_2\text{—N—CO—CH=CHCO}_2\text{H} \qquad (1a)$$

where R_{30} is oleyl derived from crude oleic acid.

To the compound of formula 1a,95 g of dodecylbenzene sulphonic acid are added together with 250 mls of odourless Kerosene to form the emulsifier composition of Example 1.

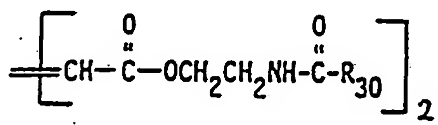
Example 2

Under an atmosphere of nitrogen, 61 g of monoethanolamine are added to 300 g of a commercial tall oil fatty acid.

The reaction is then heated up to 160°C under reflux. Water is

allowed to distill out when the temperature falls below 150°C. When 18 g of water has been removed the reaction is cooled and discharged to yield 343 g of the monoethanolamide.

Under an atmosphere of nitrogen, 300 g of the alkanolamide prepared above, are heated to 80°C and 42.9 g of maleic anhydride are added at such a rate so as to keep the temperature below 100°C. The reaction mixture is then heated to 160°C under vacuum for six hours. The reaction is then cooled and discharged to yield 335 g of the compound of formula 2a



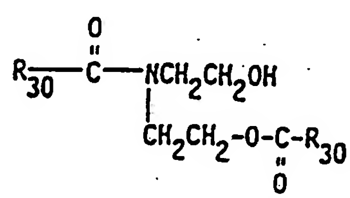
(2a)

where R_{30} is oleyl derived from tall oil fatty acid.

To the compound of formula 2a, 80 g of oxidised tall oil and 200 mls of odourless Kerosene are added to form the emulsifier composition of Example 2.

Example 3

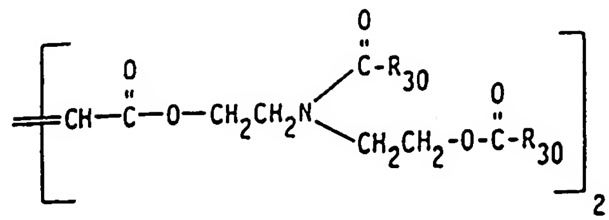
Similarly, an oleic diethanolamide is prepared by reacting 300 g tall oil fatty acid with 52.5 parts diethanolamine, to produce the 2:1 adduct of formula 3b



(3b)

This is then further reacted with maleic anhydride, according to the method of Example 2, by heating 300 g of the amide above with 21.8 g maleic anhydride.

This yield 317.8 g of a compound of the formula 3a



(3a)

To the compound of formula 3a, 40 g of oxidised tall oil and 40 g of dodecylbenzene sulphonic acid in 250 mls of odourless Kerosene are added to form the emulsifier composition of the Example 3.

Example 4

The emulsifier composition of Example 1 is used to prepare 1 laboratory barrel of mud of the following composition:

low toxic oil:	0.574	bbl
water	0.205	bbl
Calcium Chloride	31.7	ppb
Organophillic Clay. (Perchem DMB)	5.5	ppb
Barite (Barium Sulphate)	20.1	ppb
Lime	6	ppb and
Emulsifier composition	8	ppb

(ppb is pounds per barrel and bbl is barrels).

The rheology and electrical stability of the invert mud is measured initially. After hot rolling for sixteen hours at 121°C (250°F), the above tests are repeated and HTHP (high temperature high pressure) fluid loss at 121°C is measured.

Examples 5 and 6

Example 4 is repeated using an appropriate amount of the emulsifier composition of Example 2 (Example 5) or the emulsifier composition of Example 3 (Example 6).

The mud properties (especially emulsion stability and HTHP fluid loss properties) are good.

CLAIMS:

1. An emulsifier composition comprising

1) 80-99 % of the reaction product (herein defined as component 1) of

i) one or two moles of an amide-amine having at least one free amino group or a hydroxyalkyl amide having at least one free hydroxy group (herein defined as component i); component i) being free of any imidazoline groups; and

ii) one to five moles of a dicarboxylic acid or an acid anhydride (herein defined as component ii); and

2) 1-20 % of one or more compounds selected from dimer acids, C_{8-22} alkylbenzene sulphonic acids, naphthenic acids, tall oil, oxidised tall oil, C_{4-22} alkylphenol ethoxylates straight chain alcohol ethoxylates, carboxymethylates and sulphosuccinates (hereinafter defined as component 2);
all percentages of the emulsifier being based on the weight of actives in the emulsifier.

2. An emulsifier composition according to Claim 1 comprising

20-80 % of components 1 and 2 and
80-20 % of a solvent

all percentages being based by weight of the emulsifier composition.

3. An oil based well- working fluid comprising

a) 1-5 % of an emulsifier according to Claim 1 or Claim 2

b) 40-97 % of a hydrocarbon drilling oil; and
c) 2-60 % of a sodium, calcium or magnesium brine.

all percentages being by weight of the well working fluid.

4. An oil based well- working fluid according to Claim 3 in which the hydrocarbon drilling oil is diesel oil or a low toxicity drilling oil.

5. An oil based well- working fluid according to Claim 3 cr 4 in which the brine is a calcium brine.

6. An oil based well- working fluid according to any one of claims 3 to 5 in which component i) is the reaction product of

a) ethylene diamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

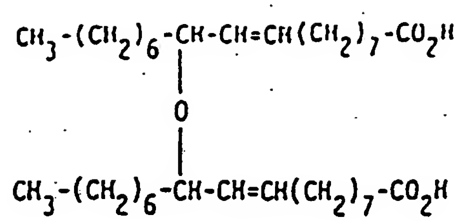
b) diethylene triamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

c) triethylene tetraamine with an C_{1-22} alkanoic acid, C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid; or

d) tetraethylene pentamine with a C_{1-22} alkanoic acid, a C_{3-22} alkenoic acid, a dimer fatty acid, a trimer fatty acid or a monoether polyacid.

7. An oil based well- working fluid according to Claim 6 in which any dimer fatty acid is of 24 to 44 carbon atoms and any trimer fatty acid is of 36 to 66 carbon atoms; and

any polyether acid contains a compound of the formula VIII



(VIII)

8. An oil based well- working fluid according to any one of claims 3 to 7 in which the dicarboxylic acids of component ii) are of the formula $HOOC-Z-CO_2H$ where Z is a direct bond, C_{1-12}alkylene or C_{2-12}alkenylene.

9. An oil based well- working fluid according to Claim 8 in which the dicarboxylic acids of component ii) are selected from itaconic acid, maleic acid, succinic acid, glutonic acid and diglycollic acid and the acid anhydrides of component ii) are selected from maleic anhydride, succinic anhydride, glutonic anhydride, diglycollic anhydride and itaconic anhydride.

10. An oil based well- working fluid according to any one of the Claims 3 to 9 in which the emulsifier composition is present in an amount to give a concentration of from 1 to 20 pounds per barrel(ppb).

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/00522

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 09 K 7/06, B 01 F 17/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 03 K 7, B 01 F 17

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X,Y	US, A, 4658036 (P. SCHILLING) 14 April 1987 see column 1, lines 6-9; column 2, lines 10-24; claims 1,2,5	1,3-6,9
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Y	EP, A, 0245157 (RHONE-POULENC) 11 November 1987 see page 2, lines 9-38; page 3, lines 1-4,22-32; page 4, lines 1-16,20-34; examples; claims 1-7	1,3-6
	--	
X	US, A, 4508628 (T.O. WALKER) 2 April 1985 see column 1, lines 5-9; column 4, lines 45-68; column 5, lines 1-50; claims 1-4	1,9
Y		3-6
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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
7th August 1989	01 SEP. 1989
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 8900522
SA 28710

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 29/08/89
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4658036	14-04-87	None		
EP-A- 0245157	11-11-87	FR-A,B	2598153	06-11-87
		AU-A-	7242787	12-11-87
US-A- 4508628	02-04-85	None		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82